"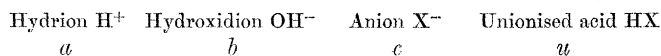 Theory of Amphoteric Electrolytes." By Professor JAMES WALKER, F.R.S., University College, Dundee. Received February 3,—Read February 18, 1904.

During the past few years considerable attention has been devoted to the behaviour of amphoteric electrolytes, *i.e.*, of substances capable of behaving as acids towards bases and as bases towards acids. The most exhaustive investigation of such substances is that by Winkelblech,[*] who determined by the customary hydrolytic methods the dissociation constants of a number of amino-acids, both with respect to their ionisation as acids and as bases.

The ionisation theory of these amphoteric electrolytes has not yet, however, been fully worked out, although the fundamental equilibrium equations have already been stated by Bredig,[†] and it is the object of this paper to present the theory from the standpoint of the law of mass action and Arrhenius's theory of electrolytic dissociation.

It is necessary first to deduce Ostwald's dilution law for simple electrolytes in the form in which we shall afterwards meet with it. When an acid, say acetic acid, is dissolved in water, the equilibrium between the ions present in the solution is expressed by means of two equations, one regulating the equilibrium between hydrion and the hydroxidion derived from the water, the other regulating the equilibrium of hydrion and the anion of the acid. Let the active masses (molecular concentrations) of the various substances involved be expressed as follows :

$$\text{Hydrion } H^+ \quad \text{Hydroxidion } OH^- \quad \text{Anion } X^- \quad \text{Unionised acid } HX$$
$$a \qquad\qquad b \qquad\qquad\qquad c \qquad\qquad u$$

then, from the law of mass action,

$$ab = K \;\dots\dots\; (1), \qquad ac = k_a u \;\dots\dots\; (2),$$

where K is the constant ionic product for water, which includes within it the constant active mass of water, and k_a is the dissociation constant of the acid. Now in order that the solution may be electrically neutral, the concentration of the positive ion must be equal to the sum of the concentrations of the negative ions, *i.e.*,

$$a = b + c \;\dots\dots\dots\dots\dots\dots\; (3)$$

Summing (1) and (2) and substituting a for $b + c$, we obtain

$$a^2 = K + k_a u \;\dots\dots\dots\dots\dots\; (4).$$

* ' Zeit. f. physikal. Chem.,' vol. 36, p. 546, 1901.
† ' Zeit. f. Elektrochemie,' vol. 6, p. 34, 1899.

For acids of moderate strength the value of a may be obtained from measurements of the electrical conductivity of the solutions, and it has been found that the results are then generally expressible by means of Ostwald's dilution formula,

$$a^2 = k_a u,$$

k_a being the dissociation constant of the acid.   For all substances accessible to direct electrical measurement, the two expressions are in practice identical, for K at $25°$ has the value 1.2×10^{-14}, whilst the product k_a u has at least the value 10^{-11}.   As far then as conductivity measurements are concerned, Ostwald's simple formula may be used instead of the strict theoretical formula.

When we consider the state of an amphoteric substance such as glycine, amino-acetic acid, $NH_2.CH_2.COOH$, in aqueous solution, it is apparent that if it acts both as acid and as base it must give rise to both hydrion H^+ and hydroxidion OH^-, the relative concentrations of which are regulated by equation (1), which holds good for all dilute aqueous solutions whatsoever.   Further, if the substance is capable of behaving as acid and as base simultaneously, the acid portion must neutralise the basic portion and form a salt.   There are two probable alternatives for the mode of neutralisation, first, the acid and the basic portion of one molecule may neutralise each other, thus

$$\begin{array}{ccc} CH_2.NH_2 & & CH_2.NH_3 \\ | & = & | \diagup \\ COOH & & COO \end{array},$$
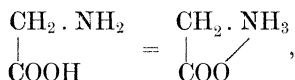
or, second, the acid portion of one molecule may neutralise the basic portion of another, thus

$$\begin{array}{ccccc} CH_2.NH_2 & HOOC & & CH_2.NH_3.OOC \\ | & + \quad | & = & | \qquad | \\ COOH & H_2N.CH_2 & & COO.NH_3.CH_2 \end{array}$$

As the former alternative is more simple than the latter, and is in accordance with known facts regarding the molecular weight of such substances in solution, we shall adhere to it in the following deductions.

Since we are unable by the methods here under discussion to distinguish between the unionised isomeric forms $NH_2.CH_2.COOH$ and $\overline{NH_3.CH_2.COO}$, and since by the law of mass action they must always exist is solution in invariable proportions, provided the temperature is constant, we may for present purposes treat them as being one and the same substance.   Similarly with regard to the hydrated form $HO.NH_3.CH_2.COOH$ formed from either of the anhydrous forms by addition of water, the mass action law leads to the conclusion that the proportion of it relatively to the total unionised glycine in the solution

must be constant.* From this hydrated form we may assume the ions to be derived. If the substance acts as base the ions produced are $NH_3.CH_2.COOH^+$ and OH^-; if it acts as acid the ions are H^+ and $OH.NH_3.CH_2.COO^-$, or the corresponding anhydrous ion $NH_2.CH_2.COO^-$. Ionisation of the internal salt would, of course, give rise to the same positive and negative ions of the glycine as those just mentioned. As a matter of fact, according to the dissociation theory, all of these ions must exist together in aqueous solution of glycine, and we shall now proceed to develope the appropriate equilibrium equations.

In general an amphoteric electrolyte H.X.OH will form the ions H^+, OH^-, $H.X^+$, and $X.OH^-$, the unionised portion being either the hydrous form H.X.OH or the anhydrous form X. Let the active masses of the various substances for equilibrium be represented as under :—

$$\begin{array}{cccccc} H^+ & OH^- & XOH^- & HX^+ & HXOH & X \\ a & b & c & d & e & f \end{array}$$
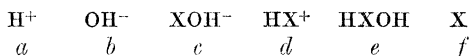
For equilibrium between the various positive and negative ions in pairs we have

$$ab = K \ \ldots \ (5), \quad ac = k'_a e \ \ldots \ (6), \quad bd = k'_b e \ \ldots \ (7), \quad cd = Qf^2 \ \ldots \ (8).$$

Here we assume for the moment that the combination of the ions c and d gives rise to the anhydrous form X, in order to show from the ionic equations that e is proportional to f, as has already been deduced from a consideration of the unionised substances alone. Multiplying (6) and (7) together we obtain

$$abcd = k'_a k'_b e^2,$$

or, substituting from (5) and (8),

$$KQf^2 = k'_a k'_b e^2,$$

i.e., the ratio of e to f is constant, the magnitudes k'_a, k'_b, K and Q being all invariable. This result, that the relative proportions of the hydrous and anhydrous forms are independent of the dilution, has already been deduced in another way by Bredig.†

Seeing now that the total unionised substance is always proportional to e, we may rewrite equations (6) and (7) in the form

$$ac = k_a u \ \ldots\ldots \ (6a), \qquad bd = k_b u \ \ldots\ldots \ (7a),$$

in which u represents the active mass of the total unionised solute. The constants k_a and k_b are, of course, different from k'_a and k'_b, and represent the dissociation constants accessible to measurement from hydrolysis experiments or the like.

---

* Compare Walker, ' Jour. Chem. Soc.,' vol. 83, p. 182 (1903).

† *Loc. cit.*

From (7a) and (5) we obtain

$$d = \frac{k_b}{K}ua \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (9).$$

From (6a) and (5) we obtain similarly

$$c = \frac{k_a}{K}ub \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (10).$$

Now the sum of the concentrations of the positive ions must be equal to the sum of the concentration of the negative ions, $i.e.$,

$$a + d = b + c,$$

or, substituting the values of c and d from (9) and (10),

$$a\left(1 + \frac{k_b}{K}u\right) = b\left(1 + \frac{k_a}{K}u\right) \quad \dots\dots\dots\dots\dots \quad (11).$$

Multiplying both sides by a, and again making use of (5), we obtain

$$a^2 = \frac{K + k_a u}{1 + \dfrac{k_b}{K}u} \dots\dots\dots\dots\dots\dots\dots\dots \quad (12),$$

or

$$a = \sqrt{\frac{K + k_a u}{1 + \dfrac{k_b}{K}u}}.$$

From equation (5) we obtain b in terms of a; the value of d is given by (9); and finally from (10) and (5) we obtain

$$c = k_a ua.$$

We are now able to express the concentrations of the various ions present in the aqueous solution of an amphoteric electrolyte if we know, as is in many cases easily possible, the concentration of the unionised substance, the dissociation constants of the substance acting as acid and base respectively, and the ionisation constant of water.

From the above formulæ it is evident in the first place that the electrical conductivity when treated in the ordinary way forms no measure of the acidity or even of the ionisation of the dissolved electrolyte, for besides hydrion there is the positive ion HX^+, the concentration of which may greatly exceed the concentration of the hydrion, and whose velocity can only be about one-fifth of the velocity of hydrion. The total conductivity is in fact the sum of four terms, each consisting of an ionic concentration multiplied into the corresponding ionic velocity. It may be seen from equation (9) that the concentrations of the two positive ions are equal when $u = K/k_b$. If the ionised

proportion is small compared with the unionised, then u is approximately equal to $1/v$, where v is the number of litres in which one gramme-molecule is dissolved, and the concentrations of the positive ions will become equal when v is approximately equal to k_b/K. At greater dilutions a is greater than d; at less dilutions d is greater than a.

In order to see clearly how different an amphoteric electrolyte is in its conductivity relations from a simple electrolyte, whether acid, base, or salt, we may consider the case for which $k_a = k_b$, *i.e.*, where the substance is of the same strength as acid and as base. From (11) we deduce $a = b$, and since from (5) the product ab is constant for all dilute solutions, it follows that the concentration of hydrion and hydroxidion is equal to the concentration of these ions in pure water, *i.e.*, the substance is at all dilutions absolutely neutral. Its solutions, therefore, behave in this respect like those of a neutral salt, but differ from them in the effect of dilution on the molecular conductivity. From (9) and (10) namely, we find that $c = d$, and that $c + d$ is proportional to u, since a is here constant. The ionised proportion is thus a constant fraction of the total dissolved substance independently of the concentration, and consequently the molecular conductivity is independent of the dilution. Comparing different substances of this type with each other, the proportion ionised is seen to vary directly as k. If a substance at $25°$ had $k_a = k_b = 1.2 \times 10^{-7}$, that is, if the acidic and basic constants were more than 100 times less than those of acetic acid or ammonia, the value of d derived from (9) would be $1.1u$, or the substance would be ionised to the extent of 52 per cent. at all dilutions, and therefore a good electrolyte.

Comparing generally the expression $a^2 = \dfrac{K + k_a u}{1 + \dfrac{k_b}{K} u}$ deduced for an amphoteric electrolyte, with the expression $a^2 = K + k_a u$ deduced for a simple acid with the same acid constant, we see that the former is equal to the latter divided by $1 + \dfrac{k_b}{K} u$. When $k_b = 0$, that is, when the electrolyte has no basic character, the divisor becomes equal to unity, and the expression for a simple acid is obtained. When k_b/K and u have finite values, it is obvious that the amphoteric electrolyte cannot strictly obey Ostwald's dilution law. If, however, either k_b/K or u is very small, Ostwald's dilution law is approximately followed, for then the values of a from the simple and amphoteric formulæ become nearly equal, and the expression $d = \dfrac{k_b}{K} ua$ for the concentration of the other positive ion nearly vanishes. The smaller the basic dissociation constant, then, and the greater the dilution, the more likely is the amphoteric electrolyte to follow the dilution law characteristic of simple acids and bases.

Prof. J. Walker.   [Feb. 3,

Of the amphoteric substances measured by Winkelblech[*] all show a ratio k_b/K at least equal to 100. In order then that the expression $\frac{k_b}{K} u$ should become small in comparison with unity, the concentration of the unionised substance (which is roughly equal to the total concentration for the compounds he investigated) must be of the order 10^{-4}, that is, v must be of the order 10,000. Solutions of feeble electrolytes having this dilution are practically beyond our ordinary means of measurement of electrical conductivity, so that we may conclude that at customary dilutions the amphoteric electrolytes studied by Winkelblech cannot give a dissociation constant when the values of the conductivity are treated in the ordinary way. This conclusion is in accordance with Winkelblech's electrical measurements, from which he endeavoured in five instances to calculate a dissociation constant. The values he obtained at different dilutions varied for each substance from 20 to 50 per cent.

In order to exhibit the effect of the presence of even feebly marked basic character in an amphoteric acid, I have calculated the concentrations of the positive ions H^+ and HX^+ for substances possessing the acid constant $k_a = 10^{-5}$ and basic constants $k_b = 1\cdot2 \times 10^{-14}$, $1\cdot2 \times 10^{-13}$, $1\cdot2 \times 10^{-12}$, and $1\cdot2 \times 10^{-11}$ respectively, the corresponding ratios k_b/K at $25°$ being 1, 10, 100, and 1000. The calculation was made for the most part by approximation, it being assumed in the first instance that the total concentration was equal to the concentration of the unionised substance. A second approximation in which the value of u obtained from the first calculation was adopted usually sufficed. If a great many dilutions have to be calculated, the employment of graphical methods may effect a saving of time.

In the following table all values of a and d have been multiplied by 10^5. For comparison, the values for $k_b/K = 0$, i.e., for a simple acid have been added.

$$k_a = 10^{-5}.$$

$v.$	$k_b/K = 0.$		$k_b/K = 1.$		$k_b/K = 10.$		$k_b/K = 100.$		$k_b/K = 1000.$	
	$a.$	$d.$	$a.$	$d.$	$a.$	$d.$	$a.$	$d.$	$a.$	$d.$
1	316	0	224	223	95·3	943	31·5	3050	9·99	9091
10	100	0	95	8·5	70·5	69·5	30·1	291	9·94	904
100	31·2	0	31·0	0·3	29·7	2·9	22·1	21·0	9·49	86
1000	9·5	0	9·5	0·0	9·4	0·1	9·06	0·8	6·79	6

The values of a for a given dilution fall off as k_b increases, and that

* *Loc. cit.*, p. 587.

the more rapidly as the dilution is small. It will be noticed that d varies with the dilution much more rapidly than a, which for high values of k_b becomes nearly independent of the dilution. What is most deserving of attention is that although for $k_b/K = 1000$ the value of the acid constant k_a is still nearly a million times greater than the value of the basic constant k_b, the acidity of the amphoteric substance is greatly diminished at small dilutions, being for example, at $v = 10$ only one-tenth of that of a simple acid with the same constant. Although the concentration of the chief conducting ion of acids is thus greatly diminished, this diminution may be more than compensated by the comparatively great concentrations of the slower ion HX^+ which appear at the same low dilutions.

With regard to the negative ions OH^- and XOH^-, it may be seen from (5) that in the cases above considered b cannot exceed the value 10^{-10}, and may thus be neglected in comparison with the other ions. It follows that the concentration of the remaining negative ion c is equal to the sum of the concentrations of the positive ions, viz., $a + d$.

All calculations made from the conductivities of solutions of amphoteric electrolytes have hitherto proceeded on the assumption that the same method of treatment might be adopted as that applicable to simple electrolytes. This is, as we see, far from being the case, and we may now consider what manner of results amphoteric electrolytes with the above constants would yield if their conductivities were treated in this erroneous fashion. Perhaps this is rendered most clearly apparent by calculating what values the Ostwald dissociation " constant " would assume at different dilutions when deduced by the ordinary process from the conductivities.

The molecular conductivity μ_∞ corresponding to H^+, XOH^- at infinite dilution may be taken as from 350—370 at 25° when referred to reciprocal Siemens units. The molecular conductivity of HX^+, XOH^- under the same conditions would be 60—70. From every concentration of HX^+, then, we may obtain a concentration of H^+ having equal conducting power, by dividing d by a number varying from 5 to 6 according to the substance considered. If we add this quotient to the real value of a we obtain a false value α, which is assumed as the value of a in the simple calculation of the dilution constant. The subjoined table contains the values of the apparent Ostwald dilution constant k_o for the amphoteric electrolytes considered above when calculated in the customary way from the values $\alpha = a + d/5$ and $\alpha = a + d/6$. In each case the constant has been multiplied by 10^5.

For $k_b/K = 1$ it will be observed that a fairly good constant k_o may be got, the values for the greater dilutions approximating within the limits of experimental error to the true value k_a. For $k_b/K = 10$ the values of k_o are no longer even approximately constant, increasing rapidly with the dilution to attain a value at $v = 1000$ approaching

$k_o \times 10^5$ calculated from $z = a + d/5$ and $z = a + d/6$.

$v.$	$k_b/K = 0.$		$k_b/K = 1.$		$k_b/K = 10.$		$k_b/K = 100.$		$k_b/K = 1000.$	
	$a+d/5.$	$a+d/6.$	$a+d/5.$	$a+d/6.$	$a+d/5.$	$a+d/6.$	$a+d/5.$	$a+d/6.$	$a+d/5.$	$a+d/6.$
10	1·0	1·0	0·944	0·938	0·718	0·679	0·780	0·622	3·30	2·62
100	1·0	1·0	0·992	0·991	0·947	0·940	0·710	0·672	0·73	0·58
1000	1·0	1·0	0·993	0·993	0·991	0·988	0·936	0·930	0·69	0·65

the true value. For $k_b/K = 100$ we have in the ordinary range of dilutions a fall to a minimum for k_o, which is apparent when $\alpha = a + d/5$ is used, and also occurs between $v = 10$ and $v = 100$ when $\alpha = a + d/6$ is employed. In this case k_o at $v = 1000$ is about 7 per cent. beneath the true value of k_a. Finally, with $k_b/K = 1000$ the value of k_o at $v = 10$ greatly exceeds the true value, and falls very rapidly with the dilution to reach a minimum at high dilutions which will generally appear in the usual range investigated. Here k_o at $v = 1000$ is 30—35 per cent. short of the true value.

For other values of k_a than that used in the above calculations the change in the value of k_o with the dilution is similar, because, as may be deduced from the formulæ on pp. 157—158, the relative values of α for two electrolytes with the same k_b do not vary greatly with the dilution, being at all dilutions approximately proportional to the square roots of the acid constants as long as u does not differ sensibly from $1/v$.

Turning now to the experimental data, we find that Ostwald obtained for ortho-amino-benzoic acid, $1 : 2\text{-}NH_2C_6H_4COOH$, values of k_o which steadily increased with increasing dilution,* confirmation of this result being subsequently furnished by Winkelblech.† Their numbers are given in the following table :—

	k (Ostwald).	k (Winkelblech).
64	0.66×10^{-5}	0.65×10^{-5}
128	0·74	0·74
256	0·84	0·84
512	0·92	0·91
1024	0·96	0·97

Ostwald accounted for the rise in the value of the constant by adopting a suggestion of Wislicenus, that double molecules might be formed according to the scheme referred to on p. 156, and that the breaking up of these double molecules at increasing dilutions into simple ionisable molecules would occasion a greater increase of ionisa-

* Ostwald, 'Zeit. für physikal. Chem.,' vol. 3, p. 261 (1889).
† Winkelblech, *loc. cit.*, p. 564.

tion as dilution progressed than that corresponding to Ostwald's dilution law. This assumption, however, is unnecessary, the theoretical discussion already given being competent to explain the facts.

The increase in the value of k_o in the range of dilution examined is obviously of the same order as that calculated for $k_b/K = 100$. We should therefore expect to obtain from hydrolysis experiments conducted with the hydrochloride of the amino-acid a value for the ratio approximating to this number. Winkelblech found from the catalysis of methyl acetate $k_b/K = 112$ in excellent accordance with the theory. He also determined the same ratio from the conductivity of solutions of the hydrochloride and obtained the divergent value 164. The same discrepancy was observed with most of the other substances he examined. If we consider, however, that the catalysis method measures the concentration of one ion only, viz., hydrion, whilst the conductivity method is concerned with a complex equilibrium among at least five kinds of ions, we see that the former is likely to yield the more accurate results. This view receives confirmation from Winkelblech's own data. For the few substances with which there is agreement between the catalysis and conductivity methods, it is found that the latter gives concordant values for the ratio at all dilutions. Where, on the other hand, the two methods do not yield the same result, there are also wide divergences amongst the values of the ratio derived from the conductivities at different dilutions. The presumption, therefore, is that the catalysis method is more trustworthy than the other. It may be noted in general that the discrepancy is great for monobasic amphoteric acids when the acid constant is great.

Knowing the ratio k_b/K, the value of k_a, and the speeds of the various ions, it is possible to calculate the molecular conductivity, and from this the apparent Ostwald dilution constant k_o. If we take from the preceding table 0.96×10^{-5} as the value of k_o at $v = 1000$, we obtain 1.02×10^{-5} as the approximate value of k_a, since the table on p. 162 shows that k_a exceeds k_o by 6—7 per cent. With regard to the speeds of the ions we may adopt Winkelblech's value $\mu_\infty = 357$ as the sum of the velocities of hydrion and the anion. There is less certainty as to the sum of the velocities of kation and anion. The velocities attributed by Winkelblech to the kation in this and in similar instances are, in my opinion, considerably overestimated. For the amino-benzoic acids he does not give directly the experimental data from which he estimated the velocity of the kations, but presumably the values were obtained by the same method as that which he adopted for other substances, viz., by measurement of the conductivity of the hydrochloride in presence of excess of base.[*] Owing to the very considerable hydrolysis of such substances in aqueous solution, the results obtained for μ at the experimental dilutions

* Compare Bredig, ' Zeit. für physikal. Chem.,' vol. 13, p. 214 (1894).

must be somewhat too high, and in consequence the speed of the kation is estimated at too high a figure. In order to proceed in a systematic way, I have added 6 in each case to the anion values found by Winkelblech for the amino-benzoic acids, and adopted the figures so obtained as the kation velocities in the succeeding calculations. The value of μ_∞ thus estimated is about 7 per cent. below that obtained by adopting Winkelblech's velocity for the kation. For the ortho-acid we have $\mu_\infty = 32 + 38 = 70$.

Calculating with these constants, we arrive at the values given in the following table :—

o-Amino-benzoic Acid, $1 : 2\text{-}NH_2.C_6H_4.COOH$.

$k_b/K = 112$, $k_a = 1\cdot02 \times 10^{-5}$, $\mu_\infty H^+,XOH^- = 357$, $\mu_\infty HX^+,XOH^- = 70$.

$v.$	$a.$	$d.$	μ calc.	μ expt.	k_o calc.	k_o (O.).	k_o (W.).
64	$23\cdot9 \times 10^{-5}$	$40\cdot1 \times 10^{-5}$	$7\cdot26$	$7\cdot21$	$6\cdot6$	$6\cdot6$	$6\cdot5$
128	$20\cdot3$	$17\cdot0$	$10\cdot8$	$10\cdot8$	$7\cdot4$	$7\cdot4$	$7\cdot4$
256	$16\cdot3$	$6\cdot7$	$16\cdot1$	$16\cdot2$	$8\cdot3$	$8\cdot4$	$8\cdot4$
512	$12\cdot3$	$2\cdot5$	$23\cdot3$	$23\cdot6$	$8\cdot9$	$9\cdot1$	$9\cdot2$
1024	$9\cdot0$	$0\cdot88$	$33\cdot5$	$33\cdot7$	$9\cdot5$	$9\cdot7$	$9\cdot6$

The experimental values of the molecular conductivity μ are the means of the concordant series of Ostwald and Winkelblech. It will be seen that the agreement between these and the calculated values is very close. For comparison the "constants" $k_o \times 10^6$ derived from the calculated and the experimental values of μ have been added.

The conductivities of solutions of para-amino-benzoic acid have been measured by the same observers, and Winkelblech determined the ratio k_b/K, which he found by the catalytic method to be 210. With this constant the value of k_a appears to be nearly 10 per cent. above the value of k_o at $v = 1000$. Adopting for the latter the mean of the numbers found by Ostwald and Winkelblech, viz. $1\cdot11 \times 10^{-5}$, we obtain $k_a = 1\cdot21 \times 10^{-5}$.

p-Amino-benzoic Acid, $1 : 4\text{-}NH_2.C_6H_4.COOH$.

$k_b/K = 210$, $k_a = 1\cdot21 \times 10^{-5}$, $\mu_\infty H^+,XOH^- = 356$, $\mu_\infty HX^+,XOH^- = 68$.

$v.$	a	$d.$	μ (calc.)	μ (O.)	μ (W.)	k_o (calc.)	k (O.)	k_o (W.)
32	$22\cdot3 \times 10^{-5}$	$138\cdot7 \times 10^{-5}$	$5\cdot55$	—	$5\cdot43$	$7\cdot7$	—	$7\cdot4$
64	$20\cdot9$	$64\cdot4$	$7\cdot55$	$7\cdot53$	$7\cdot49$	$7\cdot2$	$7\cdot2$	$7\cdot1$
128	$18\cdot7$	$28\cdot7$	$11\cdot00$	$10\cdot86$	$11\cdot12$	$7\cdot7$	$7\cdot5$	$7\cdot9$
256	$15\cdot8$	$12\cdot0$	$16\cdot47$	$16\cdot34$	$16\cdot84$	$8\cdot8$	$8\cdot7$	$9\cdot1$
512	$12\cdot5$	$4\cdot64$	$24\cdot37$	$24\cdot24$	$26\cdot29$	$9\cdot8$	$9\cdot8$	$10\cdot6$
1024	$9\cdot4$	$1\cdot70$	$35\cdot40$	$35\cdot01$	$36\cdot86$	$10\cdot7$	$10\cdot5$	$11\cdot7$

The values of μ calculated from the theory agree very well with those found by Ostwald, somewhat less well with those of Winkelblech. The most interesting point about the "constant" k_o is that there is a minimum in both the calculated and experimental values at $v = 64$.

The experimental data for meta-amino-benzoic acid are not so satisfactory as those for the isomeric acids just considered. Ostwald and Winkelblech found widely divergent values of the conductivity. Since in the following calculations use is made of Winkelblech's constants, the comparison of conductivities can only be effected with his numbers. The value of k_b/K found by the hydrolysis method is in round numbers 1100. This involves an addition of over 30 per cent. to k_o at $v = 1000$ in order to arrive at an approximate value of k_a, which in this case comes to be 1.4×10^{-5}.

m-Amino-benzoic Acid, 1 : 3-$NH_2.C_6H_4.COOH$.

$k_b/K = 1100$, $k_a = 1.4 \times 10^{-5}$, $\mu_\infty H^+, XOH^- = 355$, $\mu_\infty HX^+, XOH^- = 66$.

v.	a.	d.	μ calc.	μ (W.).	k_o calc.	k_o (W.).
64	10.9×10^{-5}	163.0×10^{-5}	9.36	9.36	11.1	11.2
128	10.6	79.2	11.51	11.72	8.5	8.8
256	9.99	36.2	15.20	16.04	7.5	8.4
512	9.07	16.5	22.06	23.04	8.0	9.1
1024	7.73	6.88	32.77	35.24	9.2	10.7

Here it will be noted that the agreement is by no means so close as in the previous instances. This is probably connected with the fact that the meta-acid rapidly oxidises in contact with platinum electrodes, and assumes a dark brown colour. The effect of this oxidation would be most apparent in the dilute solutions. Notwithstanding the want of exact accordance, the run of the constants is similar, both the values calculated from the theory and the values given by Winkelblech exhibiting a minimum at $v = 256$.

These instances exhaust the data in Winkelblech's paper for which an exact comparison of the theory with experiment is possible. They cover a range for k_b/K of 110—1100, and in each case the peculiarities of the "constants" are faithfully reproduced by the theory. An experimental investigation of some other substances to which the theory is applicable is at present in progress, and I hope in a future paper to communicate the results obtained.